METHOD AND COMPOSITION TO ENHANCE WETTING OF ECP ELECTROLYTE TO COPPER SEED

Field of the Invention

[001] The present invention relates to electrochemical plating (ECP) processes used to deposit metal layers on semiconductor wafer substrates in the fabrication of semiconductor integrated circuits. More particularly, the present invention relates to a composition and method for enhancing wetting of electrochemical plating electrolyte to a metal seed layer in electrochemical plating of metals, particularly copper, on a substrate.

Background of the Invention

[002] In the fabrication of semiconductor integrated circuits, metal conductor lines are used to interconnect the multiple components in device circuits on a semiconductor wafer. A general process used in the deposition of metal conductor line patterns on semiconductor wafers includes deposition of a conducting layer on the silicon wafer substrate; formation of a photoresist or other mask such as titanium oxide or silicon oxide, in the form of the desired metal conductor line pattern, using standard lithographic techniques; subjecting the wafer substrate to a dry etching process to remove the conducting layer from the areas not covered by the mask, thereby leaving the metal

layer in the form of the masked conductor line pattern; and removing the mask layer typically using reactive plasma and chlorine gas, thereby exposing the top surface of the metal conductor lines. Typically, multiple alternating layers of electrically conductive and insulative materials are sequentially deposited on the wafer substrate, and conductive layers at different levels on the wafer may be electrically connected to each other by etching vias, or openings, in the insulative layers and filling the vias using aluminum, tungsten or other metal to establish electrical connection between the conductive layers.

[003] Deposition of conductive layers on the wafer substrate can be carried out using any of a variety of techniques. These include oxidation, LPCVD (low-pressure chemical vapor deposition), APCVD (atmospheric-pressure chemical vapor deposition), and PECVD (plasma-enhanced chemical vapor deposition). In general, chemical vapor deposition involves reacting vapor-phase chemicals that contain the required deposition constituents with each other to form a nonvolatile film on the wafer substrate. Chemical vapor deposition is the most widely-used method of depositing films on wafer substrates in the fabrication of integrated circuits on the substrates.

[004] Due to the ever-decreasing size of semiconductor components and the ever-increasing density of integrated circuits on a wafer, the complexity of interconnecting the components in the circuits requires that the fabrication processes used to define the metal conductor line interconnect patterns be subjected to precise dimensional control. Advances in lithography and masking techniques and dry etching processes, such as RIE (Reactive Ion Etching) and other plasma etching processes, allow production of conducting patterns with widths and spacings in the submicron range. Electrodeposition or electroplating of metals on wafer substrates has recently been identified as a promising technique for depositing conductive layers on the substrates in the manufacture of integrated circuits and flat panel displays. Such electrodeposition processes have been used to achieve deposition of the copper or other metal layer with a smooth, level or uniform top surface. Consequently, much effort is currently focused on the design of electroplating hardware and chemistry to achieve high-quality films or layers which are uniform across the entire surface of the substrates and which are capable of filling or conforming to very small device features. Copper has been found to be particularly advantageous as an electroplating metal.

[005] Electroplated copper provides several advantages over electroplated aluminum when used in integrated circuit (IC)

applications. Copper is less electrically resistive than aluminum and is thus capable of higher frequencies of operation. Furthermore, copper is more resistant to electromigration (EM) than is aluminum. This provides an overall enhancement in the reliability of semiconductor devices because circuits which have higher current densities and/or lower resistance to EM have a tendency to develop voids or open circuits in their metallic interconnects. These voids or open circuits may cause device failure or burn-in.

[006] A typical standard or conventional electroplating system for depositing a metal such as copper onto a semiconductor wafer includes a standard electroplating cell having an adjustable current source, a bath container which holds an electrolyte solution (typically acid copper sulfate solution), and a copper anode and a cathode immersed in the electrolyte solution. The cathode is the semiconductor wafer that is to be electroplated with metal. Both the anode and the semiconductor wafer/cathode are connected to the current source by means of suitable wiring. The electrolyte solution may include an additive for filling of submicron features and leveling the surface of the copper electroplated on the wafer. An electrolyte holding tank may further be connected to the bath container for the addition of extra electrolyte solution to the bath container.

[007] In operation of the electroplating system, the current source applies a selected voltage potential typically at room temperature between the anode and the cathode/wafer. This potential creates a magnetic field around the anode and the cathode/wafer, which magnetic field affects the distribution of the copper ions in the bath. In a typical copper electroplating application, a voltage potential of about 2 volts may be applied for about 2 minutes, and a current of about 4.5 amps flows between the anode and the cathode/wafer. Consequently, copper is oxidized at the anode as electrons from the copper anode and reduce the ionic copper in the copper sulfate solution bath to form a copper electroplate at the interface between the cathode/wafer and the copper sulfate bath.

[008] The copper oxidation reaction which takes place at the anode is illustrated by the following reaction equation:

$$Cu \text{ ----> } Cu^{++} + 2e^{-}$$

[009] The oxidized copper cation reaction product forms ionic copper sulfate in solution with the sulfate anion in the bath 20:

$$Cu^{++} + SO_4^{--} \text{ ----> } Cu^{++}SO_4^{--}$$

[0010] At the cathode/wafer, the electrons harvested from the anode flowed through the wiring reduce copper cations in solution in the copper sulfate bath to electroplate the reduced copper onto the cathode/wafer:

$$Cu^{++} + 2e^{-} \text{ ----> } Cu$$

[0011] When a copper layer is deposited on a substrate, such as by electrochemical plating, the copper layer must be deposited on a metal seed layer such as copper which is deposited on the substrate prior to the copper ECP process. Seed layers may be applied to the substrate using any of a variety of methods, such as by physical vapor deposition (PVD) and chemical vapor deposition (PVD). Typically, metal seed layers are thin (about 50-1500 angstroms thick) in comparison to conductive metal layers deposited on a semiconductor wafer substrate.

[0012] Metal seed layers deposited on a substrate may suffer from various problems such as the presence of metal oxide on the seed layer and discontinuities in the layer, as well as contamination and the formation of pits in the layer. These drawbacks cause non-uniform wetting of the electroplating electrolyte solution to the seed layer surface. Non-uniform wetting of the electrolyte solution to the seed layer causes structural defects such as pits

in the metal electroplated onto the seed layer, compromising the structural and functional integrity of the finished IC devices fabricated on the substrate.

[0013] Traditional approaches to improving the wetting of an electroplating electrolyte solution to a metal seed layer include pre-rinsing or pre-annealing of the seed layer surface. However, both of these methods achieve unsatisfactory results. Accordingly, a new and improved composition and method is needed for enhancing the wetting of an electroplating electrolyte solution to a metal seed layer in the electrochemical plating of copper or other metal on a substrate.

[0014] An object of the present invention is to provide a novel composition and method for the pre-treatment or wetting of a seed layer on a substrate prior to electroplating a metal on the seed layer.

[0015] Another object of the present invention is to provide a novel composition and method for enhancing the wetting of an electrolyte solution to a metal seed layer in the electrochemical plating of copper or other metal on a substrate.

[0016] Still another object of the present invention is to

provide a novel composition and method which results in electroplating of a metal layer substantially devoid of structural defects on a seed layer provided on a substrate and improves gap fill capability through wetting improvement.

[0017] Yet another object of the present invention is to provide a novel composition and method which substantially reduces the contact angle of an electrolyte solution on a seed layer in the electrochemical plating of copper or other metal on the seed layer.

Summary of the Invention

[0018] In accordance with these and other objects and advantages, the present invention is generally directed to a composition and method which substantially enhances the wetting of an electrolyte solution to a seed layer on a substrate in the electrochemical plating of a metal such as copper on the seed layer. The composition is an organic mixture which includes an organic acid, such as citric acid or acetic acid, and a low molecular weight ionic polymer such as an alcohol, an amine or alkyphenol alkoxylate. According to a typical method of the invention, a metal seed layer is initally deposited on the substrate. An electrochemical plating (ECP) electrolyte solution is prepared, and the organic composition mixture is dispensed as a layered

suspension into the solution. The substrate, with the metal seed layer deposited thereon, is then moved through the suspended composition mixture layer and into the ECP electrolyte solution, such that some of the composition is layered into a wetting layer on the seed layer and enhances wetting of the electrolyte solution to the metal seed layer on the substrate. The substrate is then suspended in the solution and subjected to electrochemical plating. The electroplated metal forms a layer of high structural integrity substantially devoid of pits or other structural defects across the entire surface of the seed layer.

Brief Description of the Drawings

[0019] The invention will now be described, by way of example, with reference to the accompanying drawings, in which:

[0020] FIG. 1 is a schematic of an electrochemical plating system in implementation of the present invention;

[0021] FIG. 1A is a side view of a substrate being moved through a composition mixture layer suspended in an electroplating electrolyte bath, to form a wetting layer of the composition mixture on a seed layer provided on the substrate;

[0022] FIG. 2 is a flow diagram illustrating a typical sequential flow of process steps in implementation of the method of the present invention; and

[0023] FIG. 3 is a graph, with contact angle (on the Y-axis) plotted vs. electroplating process Q-time (on the X-axis), illustrating the contact angle of electrolyte solution on a seed layer treated according to the method of the present invention, compared to the contact angle of electrolyte solution on an untreated seed layer.

Detailed Description of the Invention

[0024] The present invention has particularly beneficial utility in the wetting of an electrolyte solution to a copper seed layer on a semiconductor wafer substrate to enhance the structural quality of a copper layer electroplated onto the seed layer in the fabrication of semiconductor integrated circuits. However, the invention is more generally applicable to the wetting of electroplating electrolyte solution to metal seed layers other than copper, and is adaptable to the electroplating of metals including but not limited to copper on a substrate in a variety of industrial applications.

[0025] The present invention is generally directed to a composition and method for substantially enhancing the wetting of

an electrolyte solution on a seed layer deposited on a substrate for the subsequent electrochemical plating (ECP) deposition of a metal, particularly copper, on the seed layer. As compared to untreated control seed layers, the composition significantly reduces the contact angle of electrolyte solution on the seed layer. Consequently, the metal electroplated onto the seed layer is substantially devoid of pits and other structural defects across the entire surface of the seed layer.

[0026] The composition of the present invention includes a mixture of an organic acid, such as citric acid or acetic acid, and a non-ionic polymer such as an alcohol, an amine or an alkyphenol alkoxylate. Preferably, the non-ionic polymer is a low molecular weight (<1,000 MW) non-ionic polymer. The organic acid is present in the composition mixture in a quantity of from typically about 2 to about 20 wt. %. The non-ionic polymer is present in the composition mixture in a quantity of from typically about 0.5 to about 10 wt. %.

[0027] In one embodiment, the composition includes a mixture of an organic acid such as citric acid or acetic acid and an alkoxylated alcohol such as ethoxylated alcohol polymer. Preferably, the composition includes typically about 10 wt. % of

the organic acid and typically about 5 wt. % of the alkoxylated alcohol.

[0028] In another embodiment, the composition includes a mixture of an organic acid such as citric acid or acetic acid and an alkoxylated polymer amine such as ethoxylated diamine polymer. Preferably, the composition includes typically about 10 wt. % of the organic acid and typically about 5 wt. % of the amine.

[0029] In still another embodiment, the composition includes a mixture of an organic acid such as citric acid or acetic acid and alkyphenol alkoxylate. Preferably, the composition includes typically about 10 wt. % of the organic acid and typically about 5 wt. % of the alkyphenol alkoxylate.

[0030] Referring to FIG. 1, an electrochemical plating (ECP) system 10 suitable for implementation of the present invention includes a standard electroplating cell having an adjustable current source 12, a bath container 14, a copper anode 16 and a cathode 18, which cathode 18 is the semiconductor wafer substrate that is to be electroplated with copper. The anode 16 and cathode/substrate 18 are connected to the current source 12 by means of suitable wiring 38. The bath container 14 holds a bath 20 typically of acid copper sulfate solution which may include an

additive for filling of submicron features and leveling the surface of the copper electroplated on the substrate 18.

[0031] The ECP system 10 may further include a pair of bypass filter conduits 24, a bypass pump/filter 30, and an electrolyte holding tank 34 for the introduction of additional electrolytes into the bath container 14, as necessary. The bypass filter conduits 24 extend through the anode 16 and open to the upper, oxidizing surface 22 of the anode 16 at opposite ends of the anode 16. The bypass filter conduits 24 connect to the bypass pump/filter 30 located outside the bath container 14, and the bypass pump/filter 30 is further connected to the electrolyte holding tank 34 through a tank inlet line 32. The electrolyte holding tank 34 is, in turn, connected to the bath container 14 through a tank outlet line 36. It is understood that the ECP system 10 heretofore described represents just one example of a possible system which is suitable for implementation of the present invention, and other systems of alternative design may be used instead.

[0032] The process of the invention may be used with any formulation for the electroplating bath solution 20, such as copper, aluminum, nickel, chromium, zinc, tin, gold, silver, lead and cadmium electroplating baths. The present invention is also

suitable for use with electroplating baths containing mixtures of metals to be plated onto a substrate. It is preferred that the electroplating bath 20 be a copper alloy electroplating bath, and more preferably, a copper electroplating bath. Typical copper electroplating bath formulations are well known to those skilled in the art and include, but are not limited to, an electrolyte and one or more sources of copper ions. Suitable electrolytes include, but are not limited to, sulfuric acid, acetic acid, fluoroboric acid, methane sulfonic acid, ethane sulfonic acid, trifluormethane sulfonic acid, phenyl sulfonic acid, methyl sulfonic acid, p-toluenesulfonic acid, hydrochloric acid, phosphoric acid and the like. The acids are typically present in the bath in a concentration in the range of from about 1 to about 300 g/L. The acids may further include a source of halide ions such as chloride ions. Suitable sources of copper ions include, but are not limited to, copper sulfate, copper chloride, copper acetate, copper nitrate, copper fluoroborate, copper methane sulfonate, copper phenyl sulfonate and copper p-toluene sulfonate. Such copper ion sources are typically present in a concentration in the range of from about 10 to about 300 g/L of electroplating solution.

[0033] Referring to FIGS. 1, 1A and 2, according to the method of the present invention, a metal seed layer 19, such as copper, is

deposited on a wafer substrate 18, as indicated in step S1 of FIG. 2. The metal seed layer 19 may be deposited on the substrate 18 using conventional chemical vapor deposition (CVD) or physical vapor deposition (PVD) techniques, according to the knowledge of those skilled in the art. The seed layer 19 has a thickness of typically about 50-1500 angstroms.

[0034] As indicated in step S2 of FIG. 2, the electrochemical plating (ECP) electrolyte bath solution 20 is prepared in the bath container 14. Next, as indicated in step S3, the organic composition mixture of the present invention is prepared and then suspended as a composition suspension layer 26 in the bath solution 20. The anode 16 and substrate 18 are then immersed in the bath solution 20 and connected to the adjustable current source 12 typically through wiring 38.

[0035] As shown in FIG. 1A and indicated in step S4 of FIG. 2, the cathode/substrate 18 is immersed in the bath solution 20 by passing the substrate 18 through the composition suspension layer 26. As shown in FIG. 1A, the seed layer 19 on the substrate 18 contacts the composition suspension layer 26 and causes a wetting layer 26a to break off of the composition suspension layer 26 and adhere to the surface of the seed layer 19. This wetting layer 26a remains on the seed layer 19 during the subsequent

electroplating process. It will be appreciated by those skilled in the art that the wetting layer 26a promotes wetting of the ECP electrolyte bath solution 20 to the seed layer 19 during the electroplating process.

[0036] As indicated in step S5, a metal layer (not shown) is electroplated onto the seed layer 19 as follows. In operation of the ECP system 10, the current source 12 applies a selected voltage potential, typically at room temperature, between the anode 16 and the cathode/substrate 18. This voltage potential creates a magnetic field around the anode 16 and the cathode/substrate 18, which magnetic field affects the distribution of the copper ions in the bath solution 20. In a typical copper electroplating application, a voltage potential of about 2 volts may be applied for about 2 minutes, and a current of about 4.5 amps flows between the anode 16 and the cathode/substrate 18. Consequently, copper is oxidized typically at the oxidizing surface 22 of the anode 16 as electrons from the copper anode 16 reduce the ionic copper in the copper sulfate solution bath 20 to form a copper electroplate (not illustrated) at the interface between the cathode/substrate 18 and the copper sulfate bath 20. By promoting uniform wetting of the electrolyte bath solution 20 to the entire surface of the seed layer 19, the wetting layer 26a facilitates electroplating of the metal onto

the seed layer 19 as a continuous metal layer substantially devoid of structural deformities such as pits. Accordingly, the electroplated metal layer on the substrate 18 contributes to the fabrication of IC devices that are characterized by high structural and operational integrity.

[0037] Referring next to the graph of FIG. 3, it is indicated that the contact angle of an ECP electrolyte bath solution on a seed layer treated according to the composition and method of the present invention is less than 20%. This is compared to a contact angle of about 30~35%, with respect to control seed layers in which the seed layer is untreated prior to the electroplating process. Consequently, the metal electroplated onto the treated seed layer is substantially devoid of pits and other structural defects which would otherwise reduce the quality of IC devices fabricated in the electroplated metal layer.

[0038] While the preferred embodiments of the invention have been described above, it will be recognized and understood that various modifications can be made in the invention and the appended claims are intended to cover all such modifications which may fall within the spirit and scope of the invention.